

TITLE

[0001] IMPROVED PRIMARY BATTERY

REFERENCE TO PRIOR FILED APPLICATIONS

[0002] This patent application claims priority to U.S. Provisional Patent Application Serial Number 60/429,947 filed November 27, 2002, which is hereby incorporated by reference herein.

[0003] This patent application is related to U.S. Patent Application filed concurrently herewith, entitled "Primary Battery having Sloped Voltage Decay," which claims priority to U.S. Provisional Patent Application Serial Number 60/456,606 filed March 20, 2003, each of which is hereby incorporated by reference herein.

GOVERNMENT LICENSE RIGHTS

[0004] NONE

TECHNICAL FIELD

[0005] The present invention relates to electrochemical storage devices, more particularly lithium batteries.

BACKGROUND

[0006] The need for improved electrochemical storage batteries continues to grow as more and more portable devices permeate our society. Where life-critical devices, such as implanted medical devices, depend on both long life and a warning of impending end of life (EOL), the need is even more acute. To date, significant effort has been expended toward increasing capacity and providing an EOL warning. However, the need to achieve high capacity (e.g., over 1000 mAh/g) combined with a distinct EOL warning sufficiently early to permit safe battery replacement without the need for a second switch-over battery has heretofore not been met.

[0007] Furthermore, in many battery-powered device applications there is a need to improve battery storage capability and/or increase battery voltage to improve battery life and increase power capability.

SUMMARY

[0008] Various embodiments of the present invention provide lithium or lithium ion batteries having certain features, such as increased electrical capacity, a reliable end of life (EOL) indicator, suitability for medical implantation, long-term storage performance, and/or increased discharge voltage. One aspect of the present invention provides an additional reaction that increases useful capacity and creates an additional voltage plateau that may be used to detect EOL. Another aspect of the present invention improves storage capability by stabilizing the anode. This improvement allows the use of an electrolyte component that increases battery voltage, thereby improving the power capability of the battery.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] Fig. 1 is a plot showing discharge voltage profiles of Li/CF_x cells using several candidate electrolytes.

[0010] Fig. 2 is a voltammogram of a cell made according to the present invention, using LiBOB dissolved in ethylene carbonate (EC), propylene carbonate (PC), and diethyl carbonate (DEC) in a volumetric ratio of 15:15:70.

[0011] Fig. 3 is a voltammogram of a cell using LiPF₆ dissolved in EC, PC, and DEC in a volumetric ratio of 15:15:70.

[0012] Fig. 4 is a plot of the open circuit voltage vs. storage time of Li/CF_x cells having different electrolytes stored at 60°C.

DETAILED DESCRIPTION

[0013] PROVIDING AN EOL INDICATOR AND INCREASING USEFUL CAPACITY

[0014] An aspect of the present invention results from significant research relating to power sources for implantable medical devices, and from the discovery that using lithium bis(oxalato)borate (LiBOB) as an electrolyte component in conjunction with conventional electrolyte solvents, combined with excess available lithium in a lithium battery provides significant increased capacity and a distinguishable lower secondary discharge voltage plateau at

between about 1.6 V and 1.9 V vs. Li^+/Li lasting about 1/3 of the battery life and suitable for end of life (EOL) indication. Alternative additives such as vinylene carbonate (VC), vinyl ethylene carbonate (VEC), lithium-cyclopentadienide, lithium tetramethylcyclopentadienide, vinyl sulfolane, carbon disulfide (CS_2), and/or other lithium bis(chelato)borates may provide similar effects.

[0015] Although LiBOB offers higher thermal stability and safety as compared with LiPF_6 , LiBOB has proven to be a generally less preferred electrolyte salt as compared to LiPF_6 or LiBF_4 due to its lower conductivity when dissolved in the same solvents. However, our research has shown that, when LiBOB is used in a cell having a lithium anode with greater capacity than its cathode (e.g., carbon or fluorinated carbon), a reaction takes place at between about 1.6 V and about 1.9 V vs. Li^+/Li potential that creates extra capacity and a distinct lower discharge voltage plateau that can be used to detect EOL. It is believed that in these tests, the LiBOB, a by-product of the LiBOB, a derivative of the LiBOB, and/or an impurity in the LiBOB served as a reactant for the secondary reaction at between about 1.6 V and about 1.9 V. Unless the context indicates otherwise, as used herein, the term “LiBOB” may refer to pure LiBOB or to LiBOB containing impurities resulting from the synthesis or decomposition of LiBOB, because it is believed that the LiBOB is either a reactant or is the source of a reactant that is of interest for its ability to create an added plateau and additional useful capacity.

[0016] The battery discharge voltage profile shows the battery voltage versus the specific discharge capacity when the battery is discharged at nominal current. Unless the context indicates otherwise, as used herein, the term “battery discharge voltage” refers to the maximum battery discharge voltage after initial discharge effects are dissipated. These initial discharge effects can include unusual voltage patterns, such as a voltage spike or dip, and are generally dissipated by a 10% depth of discharge.

[0017] Fig. 1 shows Battery Voltage on the y-axis and Specific Discharge Capacity (mAh/g) on the x-axis for several candidate electrolytes tested in a Li/CF_x cell using industry standard procedures. The electrolytes not containing LiBOB included LiBF_4 dissolved in PC and 1,2-dimethoxyethane (DME) in a volumetric ratio of 3:7 (hereinafter, “PC/DME 3/7”) 108, LiPF_6 dissolved in PC/DME 3/7 112, LiPF_6 dissolved in EC/DME 3/7 116, LiPF_6 dissolved in EC/DEC

3/7 **117**, LiBF₄ dissolved in EC/DME 3/7 **120**, LiBF₄ dissolved in tetrahydrofuran (THF)/DME 5/5 **124**, and LiBF₄ dissolved in gamma-butyrolactone (GBL)/THF 3/7 **128**. All cells using LiPF₆ or LiBF₄ had a flat discharge curve and capacities similar to each other, and all exhibited a precipitous end of life at or near 800 mAh/g without providing any EOL warning.

[0018] In contrast, it may be readily seen that both of the Li/CF_x cells containing LiBOB (**100** and **104**) exhibited a secondary voltage plateau above 1.6 V. The electrolytes tested included 1.2 M LiBOB dissolved in GBL/propyl acetate (PA) 3/7 and 1.2 M LiBOB dissolved in EC/DME 3/7. The LiBOB was purchased from Chemetall, Lot SCHK 02/09, stored at room temperature under argon gas for 3.5 months, mixed with the solvents to form the two electrolytes, stored at room temperature under argon gas for 1 month, and then tested. The cell with LiBOB dissolved in EC/DME 3/7 **100** showed higher specific discharge capacity than the one using LiBOB dissolved in GBL/PA 3/7 **104**, maintaining a voltage above 2.5 V until a rapid drop to the secondary voltage plateau of about 1.9 V, and providing an additional capacity of about 304 mAh/g for a total of about 1168 mAh/g. The cell using LiBOB dissolved in GBL/PA 3/7 **104** exhibited almost as dramatic an advantage over the non-LiBOB electrolytes, with an approximate specific discharge capacity of 1000 mAh/g. Both of the cells using the electrolyte containing LiBOB **100** and **104** provide the distinctive lower voltage plateau allowing a clear end of life indicator and a specific discharge capacity greater than the theoretical capacity of 864 mAh/g for CF_{1.0}. This is particularly important in medical applications where batteries need to be changed or recharged or the device replaced before the voltage of the battery is too low to power the device. The clearly increased capacity and beneficial secondary voltage plateau in the cells containing the LiBOB is evident from **Fig. 1**.

[0019] **Fig. 2** is a voltammogram, which shows current density versus voltage, for a cell made using a graphite cathode, a lithium anode, and an electrolyte comprising 0.7 M LiBOB in EC/PC/DEC 15/15/70. The LiBOB was purchased from Chemetall, Lot SCHK 02/09, stored at room temperature under argon gas for 3 weeks, mixed with the solvents to form the electrolyte, and then tested on the same day. This test demonstrates the reduction potential of LiBOB. Specifically, the reduction trace **204** reveals a change in current density between about 1.6 and about 1.9 V, associated with the LiBOB reduction reaction that results in the lower plateau of curves **100** and **104** of **Fig. 1**. The subsequent oxidation reaction trace **200** reveals no additional

current peak occurring between about 1.6 V and about 1.9 V, indicating that the LiBOB decomposition reaction is irreversible. The working electrode was made of 90% graphite active material and 10% polyvinylidene difluoride (PVdF) binder coated on a copper substrate (10 μm thick, 23 mm x 23 mm). The graphite-coated area is 18 mm x 23 mm. The counter electrode was a 250 μm lithium metal pressed onto a copper mesh (25 mm x 25 mm). A 28 mm x 28 mm polyethylene separator was used. The cell was tested at room temperature at a scan rate of 0.1 mV/sec.

[0020] Fig. 3 is a voltammogram showing current density versus voltage for a cell using 0.7 M LiPF_6 in EC/PC/DEC 15/15/70 with no LiBOB or any similarly decomposing additive. In contrast with Fig. 2, this trace reveals no current peak above 1.0 V, confirming that the reaction that was demonstrated by Fig. 2 did not occur in this case.

[0021] In order to create a useful EOL indicator, the amount of lithium must exceed that needed to completely react with the cathode active material and/or its byproducts produced during discharge. The lithium can be in the form of lithium metal, an alloy of lithium, mixed metals containing lithium, lithium silicon, lithium silicon oxide, lithium graphite intercalation compound (LiGIC), or other lithiated carbon. If there were no lithium in excess of that needed to react with all of the active material, the lithium would be exhausted before reaching the EOL plateau. When the lithium anode is exhausted first, the battery voltage, which is the potential difference between the cathode and anode, would be the potential difference between the cathode and the negative current collector, which is substantially higher than that of lithium, yielding a very low battery voltage. This plateau would be too low to be useful for predicting EOL because when the plateau would be reached, the battery voltage would be too low to be useful.

[0022] The preferred cathode comprises fluorinated carbon (CF_x) and the preferred anode is pure lithium. This arrangement yields a 35% capacity increase over the theoretical maximum of a Li/CF_x primary battery without LiBOB. The CF_x and lithium react to form carbon. In this specific case, the reaction voltage corresponding to the added plateau is about 1.6 V to about 1.9 V. Without limiting the invention by theory, it is theorized that carbon participates in the reaction with LiBOB. If carbon is needed for reacting with the LiBOB, the source of the carbon is not limited to CF_x . The carbon be of any type known in the art and can include mixtures of

various shapes, sizes, and structures, including graphite. The carbon may be an active material component of the cathode, or may be used as a conductor within the cathode. The cathode can further comprise additional materials, such as silver vanadium oxide (SVO), which can improve the rate capability of the cell or provide other desirable characteristics. For the certain combinations of materials, such as CF_x and SVO or carbon and SVO, the discharge profile may already exhibit a plateau for indicating EOL. In such cases, when used with the present invention, added information regarding EOL may be provided by the discharge profile, indicated by an additional plateau.

[0023] While LiBOB has been demonstrated to increase capacity and provide an EOL indicator when used as the only salt in the electrolyte, LiBOB can be used to produce these effects when used with one or more additional salts. Although this has not been tested, it is anticipated that when LiBOB comprises at least 30% of the salt content of the electrolyte, these effects will be apparent, with the effects increasing with increased percentage of LiBOB.

[0024] Other additives besides LiBOB that will similarly decompose at voltages above about 1 V may also be useful for increasing specific capacity and providing a distinct secondary discharge voltage plateau useful as an EOL indicator. Further study disclosed the same type of decomposition reaction using VC, VEC, or combinations thereof, providing a reduction reaction at about between 1.5 V and the battery discharge voltage, which may be about 2.0 to over 3.5 V. Alternative additives or salts that have a reduction reaction above about 1.0 V are also candidate additives, including lithium-cyclopentadienide, lithium tetramethylcyclopentadienide, vinyl sulfolane, and carbon disulfide (CS_2). It is also anticipated that other lithium bis(chelato)borates, such as lithium bis(succinate)borate or lithium bis(tetrafluorosuccinate)borate, may similarly decompose at voltages above about 1 V, and may be similarly useful for increasing specific capacity and providing a distinct EOL indicator. This is compared with LiPF_6 in EC:DEC, which has a decomposition potential that starts around 0.8 V and is seen as a change in slope. Such a low voltage is neither useful in extending the life of the cell, nor in providing an EOL indication, as it is too low to efficiently power most devices, particularly medical devices.

[0025] A wide range of solvents may be used with the LiBOB or other decomposing additive, alone or in mixtures, including but not limited to: PC, DME, diethyl carbonate (DEC), PA, GBL,

THF, dimethylsulfoxide (DMSO), EC, ethyl methyl carbonate (EMC), and dimethylcarbonate (DMC). The electrolyte can comprise a polymer electrolyte, which may be liquid, gel, or solid.

[0026] It is believed that the additional capacity, and thus the time between indication of approaching end of life and actual end of life, can be controlled by adjusting the amount of the additives or salts, the available excess lithium, and, to some extent, the surface area of the reactive material. Batteries powering medical devices, especially implanted devices, should include an end of life indicator circuit that alerts the user to when the voltage of the battery drops to the second discharge voltage plateau. Such devices as ventricular assist devices, artificial hearts, insulin pumps, cardiac pacemakers, automatic defibrillators, and neural stimulators may be life-sustaining, and therefore the end of life indicator is considered essential in certain applications, and the excess capacity highly advantageous. The present inventors have adapted the present invention to implantable medical devices including modular power packs used for a variety of devices.

[0027] IMPROVING STORAGE AND INCREASING DISCHARGE VOLTAGE

[0028] In many applications, the life of a device is limited by the life of the battery. Therefore, there is a need for batteries that can sustain long periods of storage without losing capacity, even at high temperatures. It is not uncommon for the materials used in the battery to degrade over time. For example, if the lithium and electrolyte react during storage, the capacity of the lithium and the amount of electrolyte are reduced, which in turn reduces the life of the battery. Ideally, this reaction is minimized to prevent an ongoing degradation of the lithium, increasing its usable capacity after storage. As will be described in detail below, one aspect of the present invention provides improved battery storage capability. Another aspect increases the battery discharge voltage, thereby increasing its power capability.

[0029] Commercial Li/CF_x batteries typically use an electrolyte comprising LiBF₄ salt in a combination solvent, such as PC/DME or EC/DME. This electrolyte provides high conductivity and a very flat discharge voltage curve beneficial to the efficiency of electronics circuits, as seen in Fig. 1.

[0030] It was reported by Nobuatsu Watanabe et al., in a book entitled, "Graphite Fluoride," Elsevier, p. 89-90, that the use of dimethylsulfoxide (DMSO) as the electrolyte solvent increases the potential of a Li/CF_x battery by about 0.2 - 0.3 V. The salt was LiClO₄. This increased voltage during discharge translates into a higher power capability for the battery. However, despite the increase in battery voltage, it is suspected that DMSO did not become a popular electrolyte solvent because it continuously reacts with lithium, resulting in a high self-discharge rate. That is, batteries using DMSO have a higher self-discharge rate than similar batteries not using DMSO.

[0031] As shown in Fig. 4, our tests confirm that a Li/CF_x battery having an electrolyte composed of 1.2-M LiBF₄ in DMSO/DME 3/7 yields a quick capacity loss, shown by a rapid decrease in the open circuit battery voltage when stored at 60°C. Within less than 2 weeks, the battery voltage dropped to 0 V. In this test, the negative electrode was lithium metal having a thickness of 30 μm on a negative current collector comprising 5-μm Cu foil. The positive electrode comprised CF_x having a porosity of 40% and a coating weight of 0.0065g/cm² on a positive current collector comprising 20-μm Al foil. The electrodes were separated by a 25 μm polypropylene (PP) separator. The battery structure was of a jellyroll type described more fully in PCT Patent Application Number PCT/US03/21343 filed July 9, 2003, which is incorporated herein by reference.

[0032] When LiBF₄ was replaced by LiBOB, the open circuit voltage stabilized at about 2.8 V. The battery structure and materials were the same, but the electrodes were activated by a 1.2-M LiBOB, DMSO/DME 3/7 electrolyte instead of 1.2-M LiBF₄ in DMSO/DME 3/7. In storage at 60°C, LiBOB with DMSO provided a battery life of more than 2 months as compared to less than 2 weeks for the similar battery having LiBF₄ with DMSO.

[0033] LiBOB improves battery life in the present invention battery having a lithium-containing anode by lowering the self-discharge rate. We believe it does this by reducing the decomposition of the electrolyte. In typical lithium primary batteries, the electrolyte in the region of the lithium anode is exposed to a low potential vs. Li⁺/Li and reacts with the lithium. Ideally, this reaction creates a passivation film on the surface of the lithium that stabilizes very quickly to prevent self discharge of the battery. However, the kinetics of the formation of this

passivation film may be different depending on the electrolytes. Xu et al. previously reported that LiBOB is a superior salt for Li ion secondary batteries because it creates a passivation film on the surface of graphite, preventing PC from co-intercalating in graphite. Possibly by a similar mechanism, we believe LiBOB stabilizes the lithium metal anode by forming a passivation film that prevents DMSO from reacting with lithium, thereby allowing its use to increase voltage.

[0034] It is believed that it is the presence of LiBOB, and not the absence of a previously-used electrolyte, that stabilizes the voltage. Therefore, LiBOB may be combined with one or more other electrolyte salts for improved storage capability, and may be used in an amount just sufficient to stabilize the lithium electrode surface. In fact, once the LiBOB has reacted with the lithium to create the passivation layer, the electrolyte may contain little or no remaining LiBOB. Evidence of the former LiBOB may be present in the form of one or more byproducts of LiBOB due to its synthesis, decomposition, reaction with lithium, reaction with other salts or solvents in the electrolyte, or oxidation. The amount of LiBOB initially in the electrolyte may be as little as 10 to 20% to achieve the desired effect. The one or more other electrolyte salts may be chosen to impart another property, such as high conductivity. Using LiBOB in accordance with this invention improves thermal stability and decreases self-discharge, thereby providing longer battery life. Adding DMSO to the LiBOB-containing electrolyte in accordance with this invention provides higher power by increasing the voltage. Thus, the LiBOB allows the use of DMSO for increasing the voltage of the battery during discharge.

[0035] The specific implementations disclosed above are by way of example and for enabling persons skilled in the art to implement the invention only. We have made every effort to describe all the embodiments we have foreseen. There may be embodiments that are unforeseeable and which are insubstantially different. We have further made every effort to describe the invention, including the best mode of practicing it. Any omission of any variation of the invention disclosed is not intended to dedicate such variation to the public, and all unforeseen, insubstantial variations are intended to be covered by the claims appended hereto. Accordingly, the invention is not to be limited except by the appended claims and legal equivalents.